Development, Processing and Characterisation of Natural Rubber-Banana Fibre Composite.

Gopakumar R, Dr R Rajesh.
Noorul Islam University,
Kanyakumari, Tamil Nadu, India

Abstract: Natural fibre reinforced eco-friendly composites are becoming an attractive alternative for synthetic materials. Natural fibres are cheaper in cost, environment-friendly, renewable and bio-degradable. The properties of natural fibre reinforced polymer composites are determined by problems like poor bonding, poor wettability, and degradation at the fibre-matrix interface and the damage of the fibre during the manufacturing process. In this work, composites using short (6mm) banana fibre in a natural rubber matrix, with a 30% v/v fibre content are prepared using compression moulding at 150°C and the composites obtained evaluated for mechanical properties like tensile strength and tear strength. A total of six specimens using natural rubber as matrix and banana fibres subjected to various surface treatments as reinforcement.

The surface treatments given to the banana fibres are alkaline treatment, benzoylation, potassium permanganate treatment and the pre-impregnation in dilute rubber solution. The influence of various chemical treatments on the fibre surface and on the mechanical strength and the fibre matrix interfacial bonding of the composite studies with the analysis of the mechanical properties of the composites indicated that the treatments given to the fibres produced an improvement in tensile modules. Tear Properties obtained shows the best results were for fibres treated with Natural rubber preimpregnation followed by alkaline treatment and permanganate treatment in the order.

Keywords: India Rubber, Banana fibre, Natural fibre, Tensile Strength, Tear Strength, alkalisation, rubber-impregnation.

1. Introduction

The interest in natural fibre reinforced polymer composites as a replacement for conventional and non-biodegradable synthetic fibres is rapidly growing both in terms of their industrial application and research. The reason is they are cheap, renewable, recyclable, and biodegradable. Many lignocellulosic fibres like banana, sisal bamboo, hemp etc are more and more often applied as the reinforcement of composites[1-2].Natural fibres such as jute, hemp, sisal, pineapple, abaca and coir have been studied as reinforcement and filler in composites[1-2]. Large availability of banana fibres and its excellent tensile properties makes it a natural choice for reinforcement in composites. The objective of the work is to develop an eco-friendly, economical and durable electrometric composite reinforced by natural materials only, using natural and abundantly available materials in India. Natural rubber as matrix and banana fibre as reinforcement. Such a composite can find a lot of applications in modern industries and automobiles and will be highly economical also.

2. Literature Survey.

2.1. Banana fibre Properties.

Mechanical properties of banana-fibre cement composites were investigated physically and mechanically by Corbiere Nicollier et al [3]. The short banana fibre-reinforced polyester composite was studied by Pothan et al [4]. Reinforcing efficiency of the natural fibre depends on upon the nature and amount of cellulose and its crystallinity [5]. Components which are present in natural fibres are cellulose, hemicelluloses, lignin, pectin and waxes. Cellulose is an organic compound, a polysaccharide consisting of a linear chain of several hundred to many thousands of Beta linked D-glucose units. Formula: \(\text{C}_6\text{H}_{10}\text{O}_5\) \(n\) density: 1.5 g/cm³[6]. Hemicellulose is different from cellulose. It comprises a group of polysaccharides compiled of a combination of five and six carbon ring sugars. Lignin is a complex hydrocarbon polymer with both aliphatic and aromatic constituents and it is totally insoluble in most of the solvents and can’t be broken down into monomer units.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Fibre</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose (%)</td>
<td>63-64</td>
</tr>
<tr>
<td>Micro fibril angle</td>
<td>11</td>
</tr>
<tr>
<td>Hemi cellulose (%)</td>
<td>6-19</td>
</tr>
<tr>
<td>Lignin (%)</td>
<td>5-10</td>
</tr>
<tr>
<td>Moisture content (%)</td>
<td>10-11</td>
</tr>
<tr>
<td>Density (kg/m³)</td>
<td>1350</td>
</tr>
<tr>
<td>Lumen size (mm)</td>
<td>5</td>
</tr>
<tr>
<td>Tensile strength (MPa)</td>
<td>529-914</td>
</tr>
<tr>
<td>Youngs modulus (G)</td>
<td>27-32</td>
</tr>
</tbody>
</table>
Lignin is considered to be a thermoplastic polymer having a glass transition temperature of around 90°C and melting temperature of around 170°C [9]. It is totally amorphous and hydrophobic in nature. It is not hydrolyzed by acids, but soluble in hot alkali, readily oxidised and easily condensable with phenol [10, 11, and 12].

2.2. Natural Rubber (NR):

NR is a naturally occurring elastomer polymer of isoprene (2-methyl) butadiene. It is extracted from the latex of a tree, the Hevea brasiliensis. Chemically NR is cis1, 4 polyisoprene, a linear, long chain polymer with repeating isoprene units (C\(_{5}\)H\(_{8}\)), it has a density of 0.93 g/cm\(^3\) at 20°C. NR has a very uniform microstructure and has a very low hysteresis. Application of reinforced NR in rubber products gives the product very useful technical characteristics such as good tensile strength, tear strength, high resilience, excellent flexibility and resistance to impact and tear and low heat build-up. However, NR is less resistant to oxidation, ozone, weathering and a wide range of chemicals and solvents, mainly due to its unsaturated chain structure and no polarity. The primary effects of short fibre reinforcement on the mechanical properties of natural rubber composites include increased modules [13, 14, and 15].

Table 2. Natural rubber ingredients.

<table>
<thead>
<tr>
<th>Sl.no.</th>
<th>Content</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Hydrocarbon</td>
<td>93.3</td>
</tr>
<tr>
<td>2</td>
<td>Acetone extract</td>
<td>2.9</td>
</tr>
<tr>
<td>3</td>
<td>Protein</td>
<td>2.8</td>
</tr>
<tr>
<td>4</td>
<td>Moisture</td>
<td>0.6</td>
</tr>
<tr>
<td>5</td>
<td>Ash</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Also, natural fibres impart the composite high specific strength, a desirable fibre aspect ratio, biodegradability. They are available from natural sources and have a low cost per unit volume basis. Furthermore, the hollow nature of vegetable fibres may impart acoustic insulation or damp properties to the matrices [16]. The main obstacle that prevents the extended utilisation of the banana fibres is the lack of good adhesion of banana fibres to most polymeric matrices. The hydrophilic nature affects adhesion to a hydrophobic matrix, leading to a loss of strength. To overcome this fibre surface may be modified to promote adhesion to the matrix.

Chemical structure of NR

Several methods to modify the natural fibre like alkaline treatment, benzoylation, permanganate treatment, acetylation etc. have been proposed [17]. Pre-impregnation of the fibre with the natural rubber resin solution will also improve fibre-matrix adhesion. The mechanical properties of a fibre reinforced polymer composite depend on the properties of the bulk constituents and on the properties of the region surrounding the fibre known as the interphase. Stress transfer from the matrix to the fibre takes place at such interphase and, therefore, it is important to study its properties to better understand the performance of the composite. In this paper, the degree of mechanical reinforcement for a natural rubber matrix that can be achieved with short natural banana fibres by modifying the fibre surface by different treatments and the composite material properties are studied. The chemical surface modification of banana fibre includes alkalinetreatment, benzoylation, permanganatetreatment, preimpregnati-on in rubber solution etc.
2.3. Stress transfer at the fibre-matrix interphase.

The mechanical properties of a composite depend mainly on fibre orientation and the fibre-matrix adhesion. This is especially true for short fibre reinforced composites. The fibres are loaded through the matrix and for good performance, the load must be transferred effectively to the fibre. For that, a strong fibre/matrix bond is required. The micromechanical events that occur for a long fibre reinforced composite are not the same as those observed for a short reinforced composite [18]. In a short fibre, there are variations in stress distribution along the fibre/matrix interphase. The end effects can be neglected in the case of long fibres, but they are very important in the case of short fibre reinforced composite. Besides since the fibres are not oriented parallel to the applied loads, fibre/matrix adhesion should be considered more carefully in short fibre reinforcements.

The parameters affecting composite properties include the fibre properties and configurations, matrix properties, modifier properties, fibre volume content, the curing conditions and process parameters. For unidirectional fibre composites, the fibre content and modulus, when the load is applied along the fibre direction is governed by the rule of mixture (ROM); $E = E_f V_f + E_m V_m$, where $E_f$, $V_f$, $E_m$ and $V_m$ are the moduli and volume fractions of the fibre and matrix respectively. This rule is not applicable for a randomly oriented short fibre reinforced composite.


ISNR20 natural rubber a moderate grade rubber used for making sheets and chappals is supplied by Silverstone rubbers, Trivandrum. Density for the NR of 1gm/cc is determined. Banana fibres with an average diameter of 80±2 microns approx., are used as reinforcement fibres (6mm long). It is supplied by Shivi fibres, Coimbatore, India. Sodium hydroxide, Toluene, Potassium permanganate, Benzyl chloride, Acetone etc. used for fibre treatments are supplied by Sun Chemicals, India.

3.1. Fibre Surface treatments.

3.1.1. Alkalisation.

The fibres are treated with a sodium hydroxide aqueous solution (4% w/v) for 1hr. at 30 °C. Fibre/water ratio is kept as 1:30 w/w. The fibres then washed with distilled water until all the sodium hydroxide was eliminated, that is, the water shows no more alkalinity. It is further neutralised by adding dilute acetic acid. Subsequently, the fibres are dried at 30°C for 24hrs and at 60°C for 5hrs.


Fibres are initially given alkaline treatment in order to activate the hydroxyl groups of the cellulose and lignin in the fibres. It is then suspended in 10% NaOH and benzyl chloride (C6H5COCl) solution for 15minutes. The isolated fibres are then taken out and dried at 30°C for 24hrs and at 60°C for 5hrs.

3.1.3. Potassium permanganate treatment of alkalized fibres.

4% w/v alkaline treated fibres are soaked in 0.2% potassium permanganate solution (in 2% acetone) for 3minutes. The fibres are then washed to remove excess potassium permanganate, and then dried at 30°C for 24hrs and at 60°C for 5hrs.

3.1.4. Surface pre-impregnation with natural rubber solution.

Banana fibres are impregnated with a 2 w/w dilute rubber solution in toluene solvent. For this natural rubber in particle size is dissolved in toluene at 80°C in a steel vessel with continuous stirring for 1hr. The fibres are then immersed into this solution from 15 minutes with constant stirring. They are then removed and transferred to a flat plate and dried at 60°C for 5hrs for the toluene solvent to evaporate completely. The clogged impregnated fibres are separated and mixed with the rubber matrix.

3.2. Composite processing.

A 30% v/v fibre content rubber-banana fibre composite is chosen to determine the effect of the different surface treatments on its mechanical properties. The fibres are added to the matrix using a laboratory model two roll mill at 150°C. The mixing process performed in a step by step order. First, one-half of rubber is placed in the mill for about 5minutes. The banana fibres are spread on to this for next 5minutes. Finally, the second half rubber put into the rollers. Total mixing time is about 25minutes. The mixed batch material is then compression moulded into sheet as per ASTM requirements using a laboratory press at a pressure of 2 ton and at a temperature of 150°C for about 10minutes. The specimens for the mechanical test are obtained from these laminates as per ASTM standards.

Fig.4 (i) Untreated and (ii) alkalized cellulose fibre [7].


Fibres are initially given alkaline treatment in order to activate the hydroxyl groups of the cellulose and lignin in the fibres. It is then suspended in 10% NaOH and benzyl chloride (C6H5COCl) solution for 15 minutes. The isolated fibres are then washed to remove excess benzyl chloride and finally washed with water and dried at 30°C for 24hrs and at 60°C for 5hrs.

\[
\text{Fiber-OH} + \text{NaOH} \rightarrow \text{Fiber-O}^+\text{Na}^+ + \text{H}_2\text{O}
\]

\[
\text{Fiber-O}^-\text{Na}^+ + \text{Cl}^- \rightarrow \text{Fiber-O}^-\text{C}^+\text{Cl}^- + \text{Na}^+
\]

\[
\text{Cellulose} + H + K\text{MnO}_4 \rightarrow \text{Cellulose} + H - O - Mn - O K^+
\]

\[
\text{Cellulose} - H - O - Mn - O K^+ \rightarrow \text{Cellulose} \text{+} H - O - Mn - O K^+
\]
3.3. Mechanical properties.

The following mechanical properties are tested for rubber-fibre composite analysis, tensile strength and tear strength. Both tensile and tear tests are performed using an Instron universal testing machine model 4411, equipped with a 5kN max. capacity and blue hill software. The specimens are conditioned at 25°C and done as per ASTM standards D412, Die D and D624, Die C, respectively. The entire test specimens are cut from the laminates obtained using standard ASTM dies as above.

4. Results and Discussions.

Six samples of banana fibre are prepared, all done by compounding using a laboratory two roll rubber mill and by compression moulding.

Table 4. Test Results.

<table>
<thead>
<tr>
<th>No</th>
<th>Nomenclature.</th>
<th>Tensile Strength (MPa)</th>
<th>Tear</th>
<th>MOD 100%</th>
<th>MOD 200%</th>
<th>MOD 300%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Strength (N/mm)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>NR</td>
<td>3.6</td>
<td>13.64</td>
<td>0.56</td>
<td>0.85</td>
<td>1.28</td>
</tr>
<tr>
<td>2</td>
<td>NRBf-Na</td>
<td>4.5</td>
<td>17.53</td>
<td>1.28</td>
<td>1.31</td>
<td>1.48</td>
</tr>
<tr>
<td>3</td>
<td>NRBf-NaBCl</td>
<td>3.8</td>
<td>15.94</td>
<td>0.95</td>
<td>1.17</td>
<td>1.42</td>
</tr>
<tr>
<td>4</td>
<td>NRBf-NaKMnO4.</td>
<td>5.1</td>
<td>16.07</td>
<td>0.81</td>
<td>1.00</td>
<td>1.22</td>
</tr>
<tr>
<td>5</td>
<td>NRBf-Ipreg.</td>
<td>4.9</td>
<td>24.26</td>
<td>1.89</td>
<td>1.83</td>
<td>1.86</td>
</tr>
<tr>
<td>6</td>
<td>NRBf-Raw.</td>
<td>4.1</td>
<td>23.53</td>
<td>1.54</td>
<td>1.63</td>
<td>1.77</td>
</tr>
</tbody>
</table>

4.1. Tensile properties.

Variations in the tensile strength and the modulus of the composites are shown in the tabular column (Table 4). The tensile
strength of the natural rubber/banana fibres (70:30 v/v) composites is shown in figure 7. Maximum tensile strength is obtained for the composite with alkali pre-treated potassium permanganate banana fibre composite. An increase of 41.75% over the non-reinforced rubber specimen. This enhancement in strength is due to both mechanical and chemical interlocking between the active fibre surface and the matrix rubber. The second best tensile value is 4.9 MPa, for the rubber composite with impregnated banana fibre. (an increase of 36.1% over the rubber specimen). This is due to an improvement in the mechanical interlocking between the rubber impregnated fibre and the natural rubber matrix. A better adhesion occurs between the rubber bonded to the banana fibre surface and the matrix rubber. The third noticeable difference is for the specimen with alkali treated banana fibre, an increase of 25% over the unreinforced rubber specimen. Alkali pre-treated benzolytated fibre composite did not show any significant change in tensile values (only 5% increase), whereas the composite with untreated fibre shown an increment of 14%).

![Tensile Strength (Mpa)](image)

**Figure 7.**

![Composite specimen after Tensile Test.](image)

**Fig.8.** Composite specimen after Tensile Test.

![Die for Tensile specimen cutting.(ASTM).](image)

**Fig.9.** Die for Tensile specimen cutting.(ASTM).

4.2. Tensile Modulus.
The tensile modulus of the specimens for 100%, 200% and 300% elongation are found (Fig. 10). Composite modulus or stiffness showed an upper value for the composites using impregnated fibre and raw fibre, 45.3% and 38.2% increase in stiffness respectively over the non-reinforced rubber sample for an elongation of 300%. For 100% elongation, the same samples showed an increase of 237.5% and 175% in stiffness over rubber sample. For 200% elongation, the increments in modulus are 115.3% and 94.1% respectively.

No noticeable change in the elastic modulus is seen for composites with benzoylation and permanganate treated fibres. Bisanda et al. [19], observed that the alkalized sisal fibres (0.5% NaOH solution for 72hrs), greatly improved the wettability of the fibres, resulting in a 21% rise in the compressive strength of the composite. It is believed that this alkali treatment results in an improvement in the interfacial bonding by providing additional sites for interlocking.

It can be seen from the results (Fig. 11), the value of tear strength varies with the different fibre treatments. A noticeable increase of 78.6% is observed for the composite specimen reinforced with rubber impregnated banana fibre compared to rubber specimen without fibre. This is mainly due to the good interfacial mechanical adhesion between the matrix impregnated fibre and the matrix. In rubber impregnated fibre composite, the failure is mainly due to the matrix failure than the fibre pullout or breakage. A 72.5% Tear strength...
increase is observed for composite using untreated fibre. For others, the tear value did not show any significant change (16.9% to 28.5%).

Fig.12. Composite specimen after Tear test.

Fibre orientation and distribution is a most important characteristic which determines the composite mechanical properties like tensile strength and tear strength. It is well known that the fibre reinforcing is most efficient along the fibre axis orientation. So the strengths obtained for a continuous fibre composite will not be same as that for a discontinuous randomly oriented short fibre reinforced composite.

4.4. Chemistry of the fibre surface treatments.


The treatment of cellulose fibres with sodium hydroxide helps to modify the cellulose molecular structure. It changes the orientation of highly packed crystalline cellulose structure by removing the cementing lignin in between the microfibrils and forming an amorphous region. This provides more access to chemicals to penetrate. The cellulose micro molecules are separated by water molecules. These hydroxyl groups sensitive to alkali brakes down and are removed from the fibre structure making it more hydrophobic. The remaining reactive molecules from fibre-cell-O-Na groups between the cellulose molecular chains [20], and the active ions on the fibre surface. This active fibre surface readily makes strong bonds with the matrix rubber giving a good interfacial strength. This reduces the hydrophilic hydroxyl groups and enhances the moisture resistance property of the fibre. It also removes a certain amount of hemicellulose, lignin, wax and oil and thereby makes the fibre surface more uniform by the elimination of microvoids. This leads to an increase in the stress transfer capacity between the ultimate cells. In addition to this, it also reduces the fibre diameter and hence an increase in fibre aspect ratio (l/d). This leads to an increased fibre surface area for better adhesion with the matrix. If the alkali concentration is higher than the optimum value, the excess delignification of the fibre takes place, resulting in weakening or damage of the fibres [21,22]. The chemical treatment of the cellulose fibre cell and sodium hydroxide is shown in figure 4. It is a pictorial representation of the fibre before and after alkalinization. Treated fibres have lower lignin content partial removal of wax and oil and a rearranged crystalline cellulose order.

4.4.2. Benzylation treatment.

Benzylation treatment uses benzoyl chloride to decrease hydrophilic nature of the fibre and improves interfacial adhesion, thereby increasing the strength of the composite. It also enhances thermal stability of the fibre [23,24]. During benzylation treatment, alkali pre-treatment is employed. At this stage, extractable materials such as lignin, waxes and oil covering materials are removed and more reactive hydroxyl groups are exposed to the surface. Then the fibres are treated with benzyl chloride. OH groups of the fibres are further replaced by benzyl group and are attached to the cellulose backbone. This results in more hydrophobic nature of the fibre and improves adhesion with the matrix [25].

4.4.3. Potassium permanganate treatment of alkalized fibres.

Permanganate treatment on natural fibres is conducted by potassium permanganate (KMnO₄) in acetone solution. This treatment forms highly reactive permanganate (MnO₄⁺) ions which react with the cellulose hydroxyl groups and forms cellulose-manganate for initiating graft copolymerization. The treatment enhances the interlocking at the surface and provides better adhesion with the matrix [26]. Formation of cellulose manganate is responsible for the higher thermal stability of the fibre. It also reacts with the lignin and separates them from the fibre cell wall. It reduces the hydrophilic nature of the fibre. Higher concentration KMnO₄ (> 1%) causes excess delignification within the cellulose structure and degrades the fibre properties.

4.4.4. Fibre pre-impregnation with Natural rubber matrix.

This gives the fibre surface a rubber coating and hence increases its hydrophobic nature and a better interphase property between the two media. The interfacial bonding also increases to a great extent.

4.4.5. Abbreviations used.

1) NR : Natural Rubber.
2) NRBF-Na : Fibre treated with NaOH.
3) NRBF-NaBCI : Fibre treated with NaOH & Benzyl chloride.
4) NRBF-NaK MnO₄ : Fibre treated with NaOH & KMnO₄.
5) NRBF-Impreg. : Fibre pre-impregnated with natural rubber.
6) NRBF- Raw. : Raw fibre.

5. Managerial Implications.

5.1. Tensile Strength.

The tensile strength of the N/R Banana Fibres (70:30 v/v) composites is shown in Fig 7. The tensile strength of the rubber composite with permanganate treatment banana fibre increased by 41.7 % due to an enhancement in the mechanical and chemical interlocking at the fibre-matrix interphase. A 36.1% increase in the tensile strength is observed for the composite with rubber impregnated fibre and a 25% increase for the composite with alkalized fibre. Composites using raw fibre and benzoylated fibres yielded only a 14% & 5% increase in the tensile strengths.

5.2 Tear strength.

For the Tear strength values, a useful increase of 77.9% was observed (Fig.11) for composite with rubber impregnated fibre reinforcement compared to composite specimen without any reinforcement, due to an enhancement in the mechanical and physical adhesion between the rubber impregnated fibre and matrix. In pre-impregnated composite failure, was mainly due to the matrix than the fibre pullout or breakage. Composite with untreated fibre reinforcement also showed a noticeable improvement of 72.5% in tensile strength. This is due to the coarse, uneven and rough surface of the fry raw fibres making an interlocking mechanism with the rubber matrix. For other treated fibres, Tear strength increments of 16.9% to 28.5% are observed.

5.3. Tensile modulus.

The tensile modulus of the specimens for 100%, 200% and 300% elongation, of the composites with rubber impregnated fibres and untreated fibres (fig.10), showed a good improvement for practical applications. Up to 237.5% and 175% respectively for a 100% elongation. So these composites can find a lot of engineering and industrial applications within the dynamic loading conditions.

6. Conclusions

The mechanical behaviours of short natural banana fibre reinforced natural rubber composites are studied. The fibre matrix interaction was improved by modifying the surface properties of the fibre, first to increase the area and contact and then to expose further the cellulose microfibrils. And thus to improve fibre wetting and impregnation. The mechanical properties observed between the different fibre surface conditions and the untreated fibres showed the interface strength increased only by changing the mechanical interaction and the chemical interactions between fibre and matrix.
One important fact resulting from the fibre surface treatment and improved fibre-matrix adhesion was a considerable reduction of fibre (l/d) ratio. The mechanical properties observed did not increase in the same ratio as expected for single-fibre interfacial strength. This was attributed to the fact that the random fibre orientations resulted in lower properties that those observed for uniaxial single fibre reinforced composites. The increase in the mechanical properties ranged between 5 and 41.7% for tensile properties. In the case of the tear strength of the composite, the increase was 16.9% to 77.9%. From the study of failure mode changed from interfacial failure to matrix failure. The interface failure was mainly a frictional type failure, and only for the pre-impregnated fibres, matrix tearing and shearing was observed. The mechanical properties determined from the tensile, and tear tests exhibit a similar behaviour for each of the different fibre surface treatments but the effect of the fibre surface was more noticeable for the tear property.

Acknowledgements

The authors would like to express the support given by the Department of Mechanical Engineering, Noorullislam University, Thuckala, TN, India

References.
